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(54) Lithium ion conductive glass-ceramics and electric cells and gas sensors using the same

(57) There are provided glass-ceramics having a high lithium ion conductivity which include in mol %:

P ₂ O ₅	35 - 40%
SiO ₂	0 - 15%
GeO ₂ + TiO ₂	25 - 50%
in which GeO ₂	0 < - 50%
and TiO ₂	0 - < 50%
ZrO ₂	0 - 10%
M ₂ O ₃ (where M is one or two selected from the group consisting of Al and Ga)	0.5 - 15%
Li ₂ O	10 - 25%

and containing Li_{1+X}M_X(Ge_{1-Y}Ti_Y)_{2-X}(PO₄)₃ (where 0 < X < 0.8 and 0 < Y < 1.0) as a main crystal phase. There are also provided glass-ceramics having a high lithium ion conductivity which include in mol %

P ₂ O ₅	32 - 40%
SiO ₂	7 - 14%
TiO ₂	38 - 45%
Li ₂ O	10 - 18%

and containing Li_{1+X}Ti₂Si_XP_{3-X}O₁₂ (where X > 0) as a main crystal phase. There are also provided solid electrolyte for an electric cell and a gas sensor using the lithium ion conductive glass-ceramics, and a solid electric cell and a gas sensor using the glass-ceramics.

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Description

This invention relates to a lithium ion conductive glass-ceramics suitable for use as wholly solid electric cells, gas sensors and electrochemical devices of various types, and electric cells and gas sensors using such glass-ceramics.

Recent development in electronics has brought about high-performance electronic devices of a compact and light-weight design and, as a power source of such electronic devices, development of an electric cell of a high energy density and a long life is strongly desired for.

Lithium has the highest oxidation-reduction potential of Li/Li^+ of all metal elements and has the smallest mass per 1 mol and, therefore, lithium cell can provide a higher energy density than other types of cells. Moreover, if a lithium ion conductive solid electrolyte is used, this electrolyte can be made very thin and, therefore, a cell of a thin film can be formed and increase in energy density per unit volume can thereby be realized.

A lithium ion cell which has been realized to date uses an organic electrolyte solution as its electrolyte and this makes it difficult to achieve a cell of a compact design such as a thin film design. This lithium ion cell has additional disadvantages that it has likelihood of leakage of electrolyte solution and likelihood of spontaneous combustion. If this lithium ion cell is replaced by a cell employing an inorganic solid electrolyte, a wholly solid cell of a high reliability will be realized.

Moreover, carbon dioxide gas produced by combustion of fossil fuel is a main cause of a hothouse effect which has recently become a serious problem and it has become necessary to incessantly watch the concentration of carbon dioxide gas. Therefore, establishment of a system for detecting carbon dioxide gas is a matter of increasing importance for the maintenance of a comfortable life in the future human society.

Carbon dioxide gas detection systems which are currently in use are generally of a type utilizing absorption of infra-red ray. These systems however are large and costly and besides are very susceptible to contamination. For these reasons, studies have recently been actively made to develop a compact carbon dioxide gas sensor using a solid electrolyte. Particularly, many reports have been made about studies using a lithium ion solid electrolyte.

For realizing such gas sensor using solid electrolyte, development of a solid electrolyte which is highly conductive, chemically stable and sufficiently heat proof is indispensable.

Among known electrolytes, Li_3N single crystal (Applied Physics letter, 30(1977) P621-22), $\text{LiI-Li}_2\text{S-P}_2\text{S}_5$ (Solid State Ionics, 5(1981) P663), $\text{LiI-Li}_2\text{S-SiS}_4$ (J. Solid State Chem. 69 (1987) P252) and $\text{LiI-Li}_2\text{S-B}_2\text{S}_3$ (Mat. Res. Bull., 18(1983) 189) glasses have high conductivity of 10^{-3}S/cm or over. These materials, however, have the disadvantages that preparation and handling of these materials are difficult and these materials are not sufficiently heat proof. Particularly, these materials have the fatal disadvantage that decomposition voltage of these materials is so low that, when they are used for an electrolyte of a solid cell, a sufficiently high terminal voltage cannot be obtained.

An oxide lithium solid electrolyte does not have the above described disadvantages and has a decomposition voltage which is higher than 3V and, therefore, it has possibility of usage as a wholly solid lithium cell if it exhibits a high conductivity at room temperature. It is known in the art that conductivity in an oxide glass can be increased by increasing lithium ion concentration. However, there is limitation in increase in the lithium ion concentration even if rapid quenching is employed for glass formation and conductivity of this glass at room temperature is below 10^{-6}S/cm at the highest.

Japanese Patent Application Laid-open Publication No. Hei-8-239218 discloses a gas sensor using a thin film of a lithium ion conductive glass. The conductivity of this lithium ion conductive glass thin film is between 1.7×10^{-7} and 6.1×10^{-7} . This is not a sufficiently high value and a solid electrolyte having a higher conductivity is desired for.

There are many reports about oxide ceramics having high conductivity. For example, $\text{Li}_4\text{GeO}_4\text{-Li}_3\text{VO}_4$ exhibits conductivity of $4 \times 10^{-5}\text{S/cm}$ at room temperature (Mat. Res. Bull. 15 (1980) P1661), $\text{Li}_{1+x}\text{M}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ ($\text{M}=\text{Al, Ga, Cr}$ etc.) exhibits conductivity of $7 \times 10^{-4}\text{S/cm}$ at room temperature (J. Electrochem. Soc., 137(1990) P1023) and $\text{Li}_{1-x}\text{Al}_x\text{Ge}_{2-x}(\text{PO}_4)_3$ exhibits conductivity of $3 \times 10^{-4}\text{S/cm}$ at room temperature (Proceedings of 8th international meeting on lithium batteries, June 6-21, 1996, Nagoya, Japan, P316-317). Oxide ceramics are superior in conductivity to oxide glasses but have the disadvantages that they require a complicated and troublesome process for manufacturing and that they are difficult to form, particularly to a thin film.

In short, the prior art lithium ion solid electrolytes have the problems that they are either low in conductivity, hard to handle, hard to form to a compact design such as a thin film.

It is, therefore, an object of the invention to provide glass-ceramics which have solved these problems and exhibit a high lithium ion conductivity at room temperature.

It is another object of the invention to provide an lithium cell and a gas sensor of a high performance by utilizing such glass-ceramics.

As described above, ceramics exhibit conductivity of 10^{-4}S/cm or over at room temperature. These ceramics, however, have pores and a large grain boundary which can not be eliminated completely and existence of these pores and grain boundary results in a decrease in conductivity. If, therefore, glass-ceramics including the above crystal are provided, there will be no pores and the grain boundary will be improved and, as a result, a solid electrolyte having a higher

conductivity is expected to be provided. Besides, glass-ceramics which share a feature of glass can be easily formed into various shapes including a thin film by utilizing this feature of glass. For these reasons, glass-ceramics are considered to have practical advantages over ceramics made by sintering.

As a result of studies and experiments made by the inventor of the present invention on the basis of the above described basic concept, the inventor has succeeded in obtaining glass-ceramics having a high lithium ion conductivity in the order of 10^{-4} S/cm or over at room temperature by producing glasses including ingredients of P_2O_5 , SiO_2 , GeO_2 , TiO_2 , ZrO_2 , M_2O_3 (where M is one or two selected from the group consisting of Al and Ga) and Li_2O and causing a crystal phase of a conductive crystal $Li_{1+X}M_X(Ge_{1-Y}Ti_Y)_{2-X}(PO_4)_3$ (where $0 < X \leq 0.8$ and $0 \leq Y < 1.0$) to grow from the glasses by heat treating these glasses. The inventor has also found that a lithium cell and a gas sensor using the glass-ceramics exhibit excellent characteristics.

Lithium ion conductive glass-ceramics achieving the above described object of the invention comprise in mol %:

P_2O_5	35 - 40%
SiO_2	0 - 15%
$GeO_2 + TiO_2$	25 - 50%
in which GeO_2	$0 < - 50\%$
and TiO_2	$0 - < 50\%$
ZrO_2	0 - 10%
M_2O_3 (where M is one or two selected from the group consisting of Al and Ga)	0.5 - 15%
Li_2O	10 - 25%

and containing $Li_{1+X}M_X(Ge_{1-Y}Ti_Y)_{2-X}(PO_4)_3$ (where $0 < X \leq 0.8$ and $0 \leq Y < 1.0$) as a main crystal phase.

In one aspect of the invention, said glass-ceramics comprise in mol %:

P_2O_5	35 - 40%
SiO_2	0 - 15%
$GeO_2 + TiO_2$	25 - 45%
in which GeO_2	$0 < - 45\%$
and TiO_2	$0 - < 45\%$
ZrO_2	0 - 10%
Al_2O_3	0.5 - 15%
Li_2O	10 - 25%

and containing $Li_{1+X}Al_X(Ge_{1-Y}Ti_Y)_{2-X}(PO_4)_3$ (where $0 < X \leq 0.8$ and $0 \leq Y < 1.0$) as a main crystal phase.

In another aspect of the invention, said glass-ceramics comprise in mol %:

P ₂ O ₅	35 - 40%
SiO ₂	0 - 15%
GeO ₂ + TiO ₂	25 - 45%
in which GeO ₂	0 < - 45%
and TiO ₂	0 - <45%
ZrO ₂	0 - 10%
Ga ₂ O ₃	0.5 - 15%
Li ₂ O	10 - 25%

and containing Li_{1+X}Ga_X(Ge_{1-Y}Ti_Y)_{2-X}(PO₄)₃ (where 0 < X ≤ 0.8 and 0 ≤ Y < 1.0) as a main crystal phase.

The inventor of the present invention has further succeeded in obtaining glass-ceramics having a high lithium ion conductivity in the order of 10⁻⁴ or over at room temperature by producing glasses including ingredients of P₂O₅, SiO₂, TiO₂ and Li₂O and causing a crystal phase of a conductive crystal Li_{1+X}Ti₂Si_XP_{3-X}O₁₂ to grow from the glasses by heat treating these glasses. The inventor has found that a lithium cell and a gas sensor using these glass-ceramics exhibit excellent characteristics.

Therefore, in another aspect of the invention, there are provided lithium ion conductive glass-ceramics comprising in mol %:

P ₂ O ₅	32 - 40%
SiO ₂	7 - 14%
TiO ₂	38 - 45%
Li ₂ O	10 - 18%

and containing Li_{1+X}Ti₂Si_XP_{3-X}O₁₂ (where X > 0) as a main crystal phase.

According to the invention, there are provided lithium ion conductive glass-ceramics which exhibit a very high lithium ion conductivity in the order of 10⁻⁴S/cm or over at room temperature. In addition to having the high conductivity, the glass-ceramics made according to the invention have such an excellent formability that they can be easily formed into various shapes including a thin film, and they are thermally and chemically stable so that they are suitable for use as electrolytes of wholly solid cells, sensors and other various electrochemical devices.

In another aspect of the invention, there is provided a solid electrolyte for an electric cell characterized in that one of the above described lithium ion conductive glass-ceramics is used as said solid electrolyte.

In another aspect of the invention, there is provided a solid electric cell characterized in that one of the above described lithium ion conductive glass-ceramics is used as a solid electrolyte.

In another aspect of the invention, there is provided a solid electrolyte for a gas sensor characterized in that one of the above described lithium ion conductive glass-ceramics is used as said electrolyte.

In still another aspect of the invention, there is provided a gas sensor characterized in that one of the above described lithium ion conductive glass-ceramics is used as a solid electrolyte.

In the description to follow, the compositions of the glass-ceramics made according to the invention are expressed on the basis of compositions of oxides as in their base glasses. Reasons for selecting the above described content ranges of the respective ingredients of the respective systems and methods for manufacturing these glass-ceramics of the respective systems will now be described.

1. The glass-ceramics of the Li_{1+X}M_X(Ge_{1-Y}Ti_Y)_{2-X}(PO₄)₃ crystal phase

In the case of the glass-ceramics according to the invention having the Li_{1+X}M_X(Ge_{1-Y}Ti_Y)_{2-X}(PO₄)₃ (where 0 < X ≤ 0.8 and 0 ≤ Y < 1.0) crystal phase, the above described composition ranges have been selected because, within these composition ranges, dense glass-ceramics containing this crystal phase as a main crystal phase and exhibiting a high lithium ion conductivity at room temperature which was never attained in the prior art ceramics were obtained by heat treating base glasses of the same composition ranges. It has been found that the same crystal phase can be pre-

precipitated also in a composition range outside of the above described composition ranges but the ratio of this crystal is so low that lithium ion conductivity of this glass-ceramic is not sufficiently high for a practical use.

In the above described ingredients, the M_2O_3 ingredient (M is one or two selected from the group consisting of Al and Ga) is of a particular importance for improving the melting property and thermal stability of the glass. By the addition of 0.5 - 15% of the M_2O_3 ingredient (M = Al, Ga), the melting property and thermal stability of the glass produced are improved remarkably and, surprisingly, the glass-ceramics obtained by heat treating this glass exhibit a high conductivity in the order of 10^{-4} S/cm or over in a broad composition range. If the M_2O_3 ingredient is below 0.5%, glassification is possible but the melting property and thermal stability of the glass are insufficient whereas if the amount of this ingredient exceeds 15%, the melting property also is deteriorated and the conductivity of glass-ceramics obtained after heat treatment drops significantly to the order of 10^{-6} S/cm or below. A preferable content range of the M_2O_3 ingredient is 1 - 14% and a more preferable content range of this ingredient is 3 - 12%.

The GeO_2 ingredient is indispensable for forming glass and constituting the conductive crystal phase. As the amount of GeO_2 increases, it becomes easier to form the glass. If the amount of this ingredient is below 25%, its effect is insufficient for obtaining the desired property whereas if the amount of this ingredient exceeds 50%, precipitation of the conductive crystal phase becomes difficult. GeO_2 can be replaced by TiO_2 up to the replacement ratio of nearly 100%. By the replacement, the lithium ion conductivity improves. On the basis of these factors, the amount of GeO_2 must be 0 - 50% and the amount of TiO_2 must be 0 - <50% and the amount of $GeO_2 + TiO_2$ must be 25 - 50%. Preferable content ranges are $GeO_2 = 0 - <45\%$, $TiO_2 = 0 - <45\%$ and $GeO_2 + TiO_2 = 25 - 45\%$. More preferable content ranges are $GeO_2 = 0 - <40\%$, $TiO_2 = 0 - <40\%$ and $GeO_2 + TiO_2 = 28 - 40\%$.

The SiO_2 ingredient improves thermal stability of the base glass and contributes to solid solution of Si^{+4} ion to the crystal phase and also to improvement of the lithium ion conductivity. If, however, the amount of this ingredient exceeds 15%, the conductivity decreases rather than increases and therefore the amount of this ingredient should not exceed 15%. A preferable content range of this ingredient is 13% or below and a more preferable content range is 10% or below.

The ZrO_2 ingredient is effective for enhancing precipitation of the crystal phase. If, however, the amount of this ingredient exceeds 10%, resistivity of the base glass to devitrification drops significantly and production of a homogeneous base glass becomes difficult and, besides, the conductivity drops sharply. Therefore, the amount of this ingredient should not exceed 10%. A preferable content range of this ingredient is 8% or below and a more preferable content range is 5% or below.

Al or Ga in the composition may partially be replaced by one or more of trivalent metals such as B, In, Sc, Fe and Cr or by one or more of divalent metals such as Mg, Ca, Sr, Ba and Zn. The amount of the ingredient replaced should however not exceed 10 mol%. If the amount of the ingredient replaced exceeds it, it becomes difficult to prepare the base glass or the conductivity of the glass-ceramic drops significantly.

For improving the melting property of the glass further, other ingredient such as As_2O_3 , Sb_2O_3 , Ta_2O_3 , CdO or PbO may be added. The amount of such ingredient however should not exceed 3%. If the addition of the ingredient exceeds 3%, the conductivity decreases with the amount of addition.

A method for manufacturing the lithium ion conductive glass-ceramics of this crystal phase will now be described.

Starting materials are weighed at a predetermined ratio and mixed uniformly and the mixed materials are thereafter put in a platinum crucible and heated and melted in an electric furnace. First, gas components coming from the raw materials are evaporated at 700 °C and then the temperature is raised to 1300 °C to 1450 °C and the materials are melted at this temperature for about one to two hours. Then, the melt is cast onto a stainless steel plate to form sheet glass. The resultant glass is subjected to heat treatment within the temperature range from 600 °C to 1000 °C for twelve to twenty-four hours and lithium ion conductive glass-ceramics containing $Li_{1+x}M_x(Ge_{1-y}Ti_y)_2 \cdot x(PO_4)_3$ and exhibiting a high lithium ion conductivity thereby is provided.

2. The glass-ceramics of the $Li_{1+x}Ti_2Si_xP_{3-x}O_{12}$ (where $X > 0$) crystal phase

In the Bulletin of the Chemical Society of Japan (1978) P2559, it is reported that the composition constituting the $LiTi_2P_3O_{12}$ crystal phase is not glassified. It is reported that the four-ingredient system $Li_2O-TiO_2-SiO_2-P_2O_5$ can be glassified but its range in detail is not reported yet. Neither is there a report about glass-ceramics made from these compositions for the purpose of providing a high lithium ion conductivity.

As a result of studying the glass forming ability of the $Li_2O-TiO_2-SiO_2-P_2O_5$, it has been found that glassification is possible within the specific composition range of $P_2O_5 = 32 - 40\%$, $SiO_2 = 7 - 14\%$, $TiO_2 = 38 - 45\%$, and $Li_2O = 10 - 18\%$ (in mol%) and that glass-ceramics which precipitate, as a result of heat treatment of the base glass within this composition range, the $Li_{1+x}Ti_2Si_xP_{3-x}O_{12}$ ($X > 0$) crystal phase surprisingly has a lithium ion conductivity which is significantly higher than the glass-ceramics which have been reported to date. Further, an electric cell which uses these glass-ceramics exhibits discharge current density which is higher than the prior art cells. Likewise, a gas sensor which uses these glass-ceramics exhibits a better sensitivity than the prior art gas sensors.

There is a glassifying region other than the above described composition range but glass-ceramics of the compositions in this region produced after heat treatment do not exhibit a high conductivity. For example, in case the amount of Li_2O ingredient exceeds 30 mol%, glass can be produced easily but, after heat treatment, a large amount of a non-conductive crystal phase has been precipitated in addition to the $\text{Li}_{1+x}\text{Ti}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ ($x > 0$) crystal phase and, as a result, the conductivity drops to a value below 10^{-7} S/cm. On the basis of results of these experiments, the composition range of the glass-ceramics of the invention has been determined as described above.

A preferable composition range is one consisting of $\text{P}_2\text{O}_5 = 35 - 40\%$, $\text{SiO}_2 = 8 - 13\%$, $\text{TiO}_2 = 40 - 45\%$ and $\text{Li}_2\text{O} = 10 - 15\%$ (in mol%). A more preferable composition range is one consisting of $\text{P}_2\text{O}_5 = 35 - 38\%$, $\text{SiO}_2 = 8 - 12\%$, $\text{TiO}_2 = 40 - 45\%$ and $\text{Li}_2\text{O} = 10 - 14\%$ (in mol%).

Ti may partially be replaced by one or more of quadrivalent metals such as Zr, Hf, Ge and Sn or one or more of trivalent metals such as B, In, Sc, Fe and Cr or one or more of divalent metals such as Mg and Zn. The amount of the ingredient replaced however should not exceed 5 mol%. If the amount of the ingredient replaced exceeds 5 mol%, it becomes difficult to produce the base glass or the conductivity drops sharply.

For improving the melting property of the glass further, other ingredient such as As_2O_3 , Sb_2O_3 , Ta_2O_3 , CdO or PbO may be added. The amount of such ingredient however should not exceed 3 mol%. If the addition of the ingredient exceeds 3 mol%, the conductivity decreases with the amount of addition.

A method for manufacturing the lithium ion conductive glass-ceramics of this crystal phase will now be described.

Starting materials are weighed at a predetermined ratio and mixed uniformly and the mixed materials are thereafter put in a platinum crucible and heated and melted in an electric furnace. First, gas components coming from the raw materials are evaporated at 700°C and then the temperature is raised to 1450°C to 1500°C and the materials are melted at this temperature for about one to two hours. Then, the melt is cast onto a stainless steel plate to form sheet glass. The resultant glass is subjected to heat treatment within the temperature range from 900°C to 1100°C for about fifteen hours by using the one stage heat treatment method and lithium ion conductive glass-ceramics containing $\text{Li}_{1+x}\text{Ti}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ as a main crystal phase and exhibiting a high lithium ion conductivity thereby is provided.

In the accompanying drawings,

Fig. 1 is a graph showing an X-ray diffraction pattern of Example 1;

Fig. 2 is a sectional view of an example of a lithium cell using a lithium ion conductive solid electrolyte of Example 4;

Fig. 3 is a sectional view showing an example of a gas sensor using a lithium ion conductive solid electrolyte of Example 4;

Fig. 4 is a graph showing an effective discharge characteristic of the cell shown in Fig. 2; and

Fig. 5 is a graph showing an electromotive force characteristic by a carbonate gas partial pressure at room temperature of the gas sensor shown in Fig. 3.

Fig. 6 is a graph showing an X-ray diffraction pattern of Example 13;

Fig. 7 is a graph showing an effective discharge characteristic of the cell using the glass-ceramic of Example 14; and

Fig. 8 is a graph showing an electromotive force characteristic by a carbonate gas partial pressure at room temperature of the gas sensor using the glass-ceramic of Example 14.

Examples

Examples of the glass-ceramics made according to the invention will now be described. It should be noted that these examples are illustrative only and the scope of the invention in no way is restricted by these examples.

1. Examples of the glass-ceramics of the $\text{Li}_{1+x}\text{M}_x(\text{Ge}_{1-x}\text{Ti}_x)_2(\text{PO}_4)_3$ crystal phase

Example 1

As starting materials, $\text{NH}_4\text{H}_2\text{PO}_4$, GeO_2 , $\text{Al}(\text{OH})_3$ and Li_2CO_3 were used. These starting materials were weighed to constitute a composition of 37.5% P_2O_5 , 35.0% GeO_2 , 7.5% Al_2O_3 and 20.0% Li_2O in mol %. The materials were mixed uniformly and then put in a platinum crucible and heated and melted in an electric furnace. First, CO_2 , NH_3 and H_2O coming from the raw materials were evaporated at 700°C . Then the temperature was raised to 1300°C and the materials were melted by heating them at this temperature for 1.5 hour. Thereafter, the melt was cast onto a stainless steel plate to form a uniform sheet glass. The glass was annealed at 520°C for two hours for removing thermal stress of the glass.

The glass thus produced was cut into specimens each having the size of 20×20 mm. The specimens of glass were polished on both surfaces and subjected to heat treatment at 750°C for twelve hours and, as a result, a dense glass-ceramic was produced. The crystal phase which precipitated in the specimens was determined by the powder X-ray dif-

fraction method. As a result, it was found that the precipitated crystal phase was $\text{Li}_{1+x}\text{Al}_x\text{Ge}_{2-x}(\text{PO}_4)_3$. An X-ray diffraction pattern of this glass-ceramic is shown in Fig. 1. This glass-ceramic exhibited a high conductivity of $4.0 \times 10^{-4} \text{ S/cm}$ at room temperature.

5 Example 2

As starting materials, $\text{NH}_4\text{H}_2\text{PO}_4$, GeO_2 , Ga_2O_3 and Li_2CO_3 were used. These starting materials were weighed to constitute a composition of 37.5% P_2O_5 , 40.0% GeO_2 , 5.0% Ga_2O_3 and 17.5% Li_2O in mol %. The materials were mixed uniformly and then put in a platinum crucible and heated and melted in an electric furnace. First, CO_2 , NH_3 and H_2O coming from the raw materials were evaporated at 700°C . Then the temperature was raised to 1300°C and the materials were melted by heating them at this temperature for 1.5 hour. Thereafter, the melt was cast onto a preheated stainless steel plate to form a uniform sheet glass. The glass was annealed at 510°C for two hours for removing thermal stress of the glass.

The glass thus produced was cut into specimens each having the size of $20 \times 20 \text{ mm}$. The specimens of glass were polished on both surfaces and subjected to heat treatment at 800°C for twelve hours and, as a result, a dense glass-ceramic was produced. The crystal phase which precipitated in the specimens was determined by the powder X-ray diffraction method. As a result, it was found that the precipitated crystal phase was $\text{Li}_{1+x}\text{Ga}_x\text{Ge}_{2-x}(\text{PO}_4)_3$. This glass-ceramic exhibited a high conductivity of $2.0 \times 10^{-4} \text{ S/cm}$ at room temperature.

20 Example 3

As starting materials, $\text{NH}_4\text{H}_2\text{PO}_4$, GeO_2 , TiO_2 , Al_2O_3 and Li_2CO_3 were used. These starting materials were weighed to constitute a composition of 37.5% P_2O_5 , 30.0% GeO_2 , 10% TiO_2 , 5.0% Al_2O_3 and 17.5% Li_2O in mol %. The materials were mixed uniformly and then put in a platinum crucible and heated and melted in an electric furnace. First, CO_2 , NH_3 and H_2O coming from the raw materials were evaporated at 700°C . Then the temperature was raised to 1400°C and the materials were melted by heating them at this temperature for 1.5 hour. Thereafter, the melt was cast onto a preheated stainless steel plate to form a uniform sheet glass. The glass was annealed at 540°C for two hours for removing thermal stress of the glass.

The glass thus produced was cut into specimens each having the size of $20 \times 20 \text{ mm}$. The specimens of glass were polished on both surfaces and subjected to heat treatment at 850°C for twelve hours and, as a result, a dense glass-ceramic was produced. The crystal phase which precipitated in the specimens was determined by the powder X-ray diffraction method. As a result, it was found that the precipitated crystal phase was $\text{Li}_{1+x}\text{Al}_x(\text{Ge}_{2-y}\text{Ti}_y)_{2-x}(\text{PO}_4)_3$. This glass-ceramic exhibited a high conductivity of $2.0 \times 10^{-4} \text{ S/cm}$ at room temperature.

35 Examples 4 to 10

Specimens of Examples 4 to 10 were prepared by employing a method similar to the one employed in preparing the glass-ceramic of Example 2. Compositions and conductivity at room temperature of the respective Examples are shown in the following Tables 1 and 2.

The conductivity of the glass-ceramics was measured within a range from 10^{-2} - $3 \times 10^{-7} \text{ Hz}$ by the ac impedance. Resistance of the specimens (sum of grain resistance and grain boundary resistance) was determined from the Cole-Cole Plot and the conductivity was calculated by the equation $\sigma = (t/A)(1/R)$ (where σ is conductivity, t is thickness of the specimen, A is electrode area and R is resistance of the specimen).

Table 1

Example No.	1	2	3	4	5
P ₂ O ₅ (mol%)	37.5	37.5	37.5	37.5	37.5
SiO ₂ (mol%)					
GeO ₂ (mol%)	35.0	40.0	30.0	37.5	40.0
TiO ₂ (mol%)			10.0		
ZrO ₂ (mol%)					
Al ₂ O ₃ (mol%)	7.5		5.0	4.5	5.0
Ga ₂ O ₃ (mol%)		5.0		2.0	
Li ₂ O (mol%)	20.0	17.5	17.5	18.5	17.5
Conductivity ($\times 10^{-4}$ S/cm)	4.0	2.0	3.5	1.5	3.0

Table 2

Example No.	6	7	8	9	10
P ₂ O ₅ (mol%)	39.0	39.0	39.0	33.0	33.0
SiO ₂ (mol%)				5.0	8.0
GeO ₂ (mol%)	37.5	33.0	35.5	37.5	11.0
TiO ₂ (mol%)					30.0
ZrO ₂ (mol%)				2.0	
Al ₂ O ₃ (mol%)		11.0	6.0	4.5	5.0
Ga ₂ O ₃ (mol%)	9.0		4.0		
Li ₂ O (mol%)	14.5	17.0	15.5	18.0	14.0
Conductivity ($\times 10^{-4}$ S/cm)	1.2	2.0	1.5	2.5	5.0

Example 11

As a typical example of a lithium electric cell, an example of flat type cell using the lithium ion conductive glass-ceramic of Example 4 as a solid electrolyte is shown in the sectional view of Fig. 2. The cell is composed of a negative electrode container 6, a negative electrode collector 4 constructed of a conductive thin film or a thin film made of aluminum or stainless steel, a negative electrode 2, a lithium ion conductive glass-ceramic layer 1, a positive electrode 3, a positive electrode collector 5 constructed of a conductive thin film or a thin film made of aluminum or stainless steel, a positive electrode container 7 and an insulating filler 8 made of an insulating material such as polypropylene. The positive and negative electrodes 2 and 3 are received in the case formed by the positive and negative electrode containers 6 and 7 in such a manner that these electrodes 2 and 3 oppose each other through the lithium ion conductive glass-ceramic layer 1. The positive electrode 3 is connected to the positive electrode container 7 through the positive electrode collector 5 and the negative electrode 2 is connected to the negative electrode container 6 through the negative electrode collector 4. Chemical energy produced in the cell can be collected as electric energy from terminals of the negative electrode container 6 and the positive electrode container 7.

In constructing the cell made according to the invention, various other materials which are conventionally used for forming a cell can be used except for the solid electrolyte portion.

The lithium ion conductive glass-ceramic layer must be sufficiently thin, i.e., 1 mm or less and preferably 0.5 mm or less. Many reports and proposals have been made about the material of the positive electrode 3 and it is typically made of LiCoO₂ or Li_{1-x}V₃O₈. Likewise, reports and proposals have been made about the material of the negative electrode

2 and it is typically made of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ or carbon.

As to the positive and negative electrodes 2 and 3 formed on the opposite surfaces of the lithium ion conductive glass-ceramic layer 1 and the collectors 4 and 5 formed in the negative and positive electrodes 2 and 3, these component parts may be preformed respectively and stacked one after another to a composite cell. Alternatively, the positive and negative electrodes 2 and 3 and the collectors 4 and 5 may be formed sequentially by any of suitable known methods including ion sputtering, CVD, screen printing, coating, sol-gel method, ion plating, ion beam evaporation and electron beam evaporation.

As a comparative example, a cell is composed in the same manner as in the above example except that the solid electrolyte is formed by mixing 1.7 mol of titanium oxide, 0.7 mol of lithium carbonate, 3.0 mol of ammonium phosphate and 0.2 mol of aluminum oxide in an agate mortar, press-forming the mixture to pellets and sintering the pellets at 900 °C for two hours, crushing the sintered pellets again in an agate mortar, press-forming the crushed material which has passed a sieve of 400 mesh to pellets again, sintering the pellets at 1000 °C for two hours and processing the sintered pellets to a thin plate.

Effective discharge characteristics of the cell of Fig. 2 and the cell of the comparative example are shown in Fig. 4.

Example 12

As a typical example of a gas sensor, an example of a carbon dioxide gas sensor using the lithium ion conductive glass-ceramic of Example 4 as a solid electrolyte is shown in section in Fig. 3. The upper and lower surfaces of a lithium ion conductive glass-ceramic layer 11 are polished to provide the layer 11 having a thickness of 1 mm to 2 mm, preferably 1 mm or below and more preferably 0.5 mm or below. On one of the surfaces of the layer 11 (the upper surface in the illustrated example) is formed, by ion sputtering, a layer of metal carbonate, preferably lithium carbonate or a mixture of lithium carbonate and other carbonate. A platinum mesh 10 to which a lead 14 is connected is disposed on the surface of this metal carbonate layer to form an electrode. Then, a layer 9 of metal carbonate is formed on the upper surface of the electrode 10 to fix the electrode 10. On the other surface (the lower surface in the illustrated example) of the lithium ion conductive layer 11 is formed, by evaporation, a platinum thin film to form an electrode 12 and a lead 13 is connected to the electrode 12. According to this sensor, an electromotive force corresponding to the concentration of carbon dioxide gas is produced between the two electrodes due to dissociation equilibrium of the carbonate by the carbon dioxide gas in a mixture gas including the carbon dioxide gas and, therefore, the concentration of the carbon dioxide gas can be detected by measuring this electromotive force.

Forming of the carbonate layer and the electrode layers is not limited to the above method but these layers may be formed by other known methods including CVD, screen printing, sol-gel method, ion plating, ion beam evaporation, MBE, vacuum evaporation and electron beam evaporation.

The electromotive force characteristic by a carbonate gas partial pressure at room temperature of this glass-ceramic is shown in Fig. 5.

2. Examples of the glass-ceramics of the $\text{Li}_{1+x}\text{Ti}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ crystal phase

Example 13

As starting materials, $\text{NH}_4\text{H}_2\text{PO}_4$, SiO_2 , TiO_2 , $\text{Al}(\text{OH})_3$ and Li_2CO_3 were used. These starting materials were weighed to constitute a composition of 37.1% P_2O_5 , 9.5% SiO_2 , 40.6% TiO_2 and 12.8% Li_2O in mol %. The materials were mixed uniformly and then put in a platinum crucible and heated and melted in an electric furnace. First, CO_2 , NH_3 and H_2O coming from the raw materials were evaporated at 700 °C. Then the temperature was raised to 1450 °C and the materials were melted by heating them at this temperature for 1.5 hour. Thereafter, the melt was cast onto a preheated stainless steel plate to form a uniform sheet glass. The glass was annealed at 550 °C for two hours for removing thermal stress of the glass.

The glass thus produced was subjected to heat treatment at 1000 °C for fifteen hours and, as a result, a desired glass-ceramic was produced. The crystal phase which precipitated in the specimens was determined by the powder X-ray diffraction method. As a result, it was found that the precipitated crystal phase was $\text{Li}_{1+x}\text{Ti}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$. An X-ray diffraction pattern of this glass-ceramic is shown in Fig. 6. This glass-ceramic exhibited a high conductivity of $2.0 \times 10^{-4} \text{ S/cm}$ at room temperature.

Examples 14 to 17

Glass-ceramics of Examples 14 to 17 were prepared by employing the same method as the one employed in preparing the glass-ceramic of Example 13. The compositions and conductivity at room temperature of Examples 13 to 17 are shown in Table 3.

The conductivity of these Examples were measured by the same method as the one employed in Examples 1 to 10.

Table 3

Example No.	13	14	15	16	17
Li ₂ O (mol%)	12.8	12.8	14.8	14.8	10.8
TiO ₂ (mol%)	42.6	40.6	40.6	40.6	42.6
SiO ₂ (mol%)	9.5	9.5	7.5	9.5	11.5
P ₂ O ₅ (mol%)	35.1	37.1	37.1	35.1	35.1
Conductivity (X 10 ⁻⁴ S/cm)	2.0	1.0	6.0	5.0	5.1

Example 18

A lithium cell was produced by using the glass-ceramic of Example 14 as its solid electrolyte and using a cell structure which is the same as the cell structure of Example 11. Effective discharge characteristics of this cell and the cell of the comparative example which is the same as the comparative example employed in Example 11 are shown in Fig. 7.

Example 19

A gas sensor was produced by using the glass-ceramic of Example 14 as its solid electrolyte and using the same gas sensor structure as the one used in Example 12. Electromotive force characteristic by a carbonate gas partial pressure at room temperature of this gas sensor is shown in Fig. 8.

Claims

1. Lithium ion conductive glass-ceramics comprising in mol %:

P ₂ O ₅	35 - 40%
SiO ₂	0 - 15%
GeO ₂ + TiO ₂	25 - 50%
in which GeO ₂	0 < - 50%
and TiO ₂	0 - < 50%
ZrO ₂	0 - 10%
M ₂ O ₃ (where M is one or two selected from the group consisting of Al and Ga)	0.5 - 15%
Li ₂ O	10 - 25%

and containing Li_{1+X}M_X(Ge_{1-Y}Ti_Y)_{2-X}(PO₄)₃ (where 0 < X ≤ 0.8 and 0 ≤ Y < 1.0) as a main crystal phase.

2. Glass-ceramics as defined in claim 1 wherein said glass-ceramics comprise in mol %:

P ₂ O ₅	35 - 40%
SiO ₂	0 - 15%
GeO ₂ + TiO ₂	25 - 45%
in which GeO ₂	0 < - 45%
and TiO ₂	0 - <45%
ZrO ₂	0 - 10%
Al ₂ O ₃	0.5 - 15%
Li ₂ O	10 - 25%

and containing $\text{Li}_{1+X}\text{Al}_X(\text{Ge}_{1-Y}\text{Ti}_Y)_{2-X}(\text{PO}_4)_3$ (where $0 < X \leq 0.8$ and $0 \leq Y < 1.0$) as a main crystal phase.

3. Glass-ceramics as defined in claim 1 wherein said glass-ceramics comprise in mol %:

P ₂ O ₅	35 - 40%
SiO ₂	0 - 15%
GeO ₂ + TiO ₂	25 - 45%
in which GeO ₂	0 < - 45%
and TiO ₂	0 - <45%
ZrO ₂	0 - 10%
Ga ₂ O ₃	0.5 - 15%
Li ₂ O	10 - 25%

and containing $\text{Li}_{1+X}\text{Ga}_X(\text{Ge}_{1-Y}\text{Ti}_Y)_{2-X}(\text{PO}_4)_3$ (where $0 < X \leq 0.8$ and $0 \leq Y < 1.0$) as a main crystal phase.

4. Lithium ion conductive glass-ceramics comprising in mol %:

P ₂ O ₅	32 - 40%
SiO ₂	7 - 14%
TiO ₂	38 - 45%
Li ₂ O	10 - 18%

and containing $\text{Li}_{1+X}\text{Ti}_2\text{Si}_X\text{P}_{3-X}\text{O}_{12}$ (where $X > 0$) as a main crystal phase.

5. A solid electrolyte for an electric cell characterized in that a lithium ion conductive glass-ceramic as defined in any of claims 1 - 4 is used as said solid electrolyte.
6. A solid electric cell characterized in that a lithium ion conductive glass-ceramic as defined in any of claims 1 - 4 is used as a solid electrolyte.
7. A solid electrolyte for a gas sensor characterized in that a lithium ion conductive glass-ceramic as defined in any of claims 1 - 4 is used as said electrolyte.
8. A gas sensor characterized in that a lithium ion conductive glass-ceramic as defined in any of claims 1 - 4 is used as a solid electrolyte.

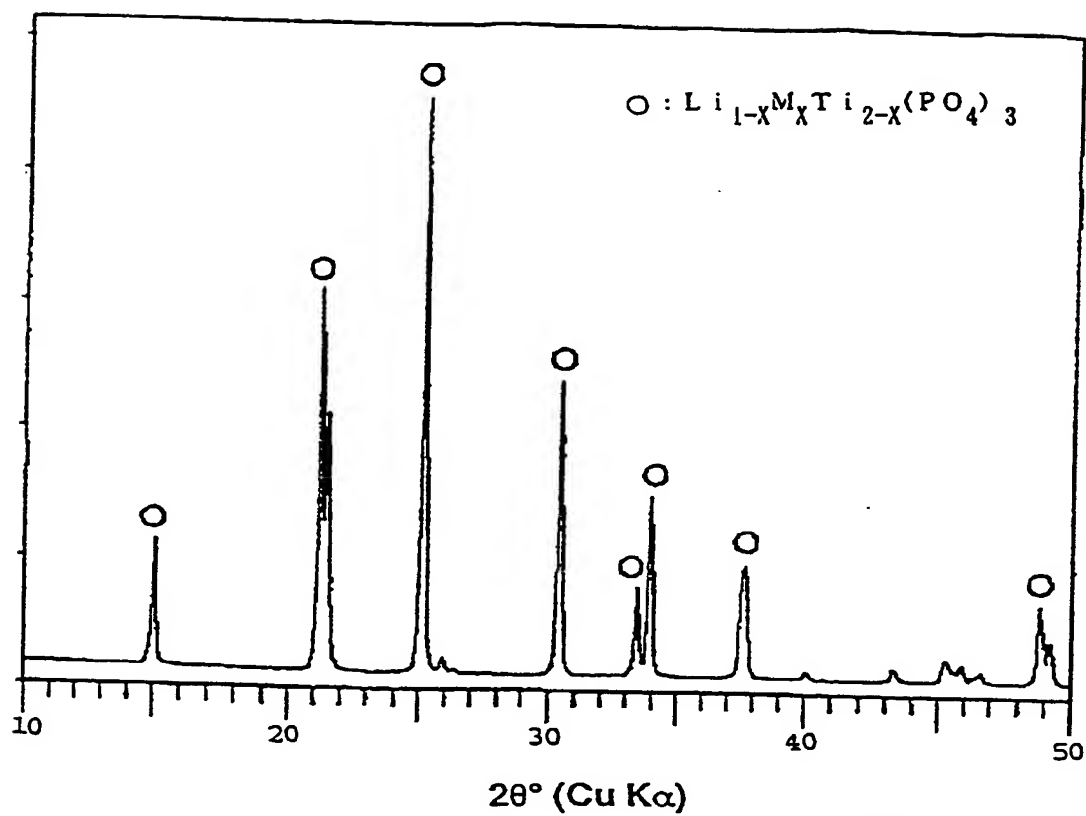


FIG. 1

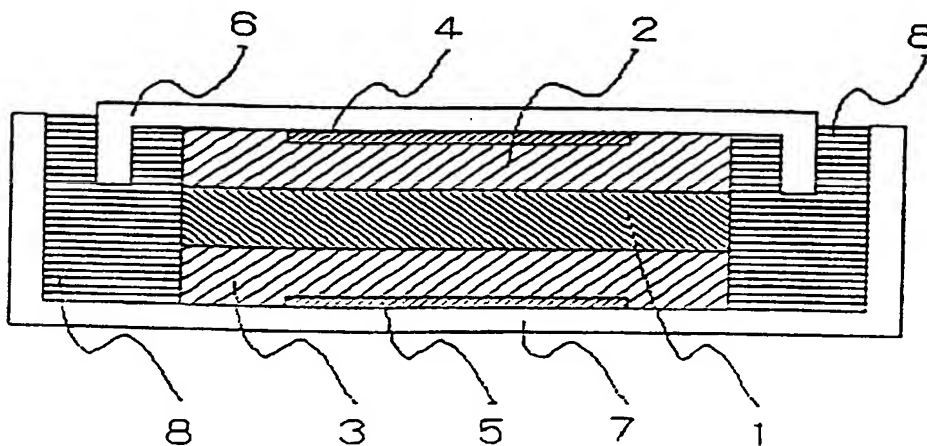


FIG. 2

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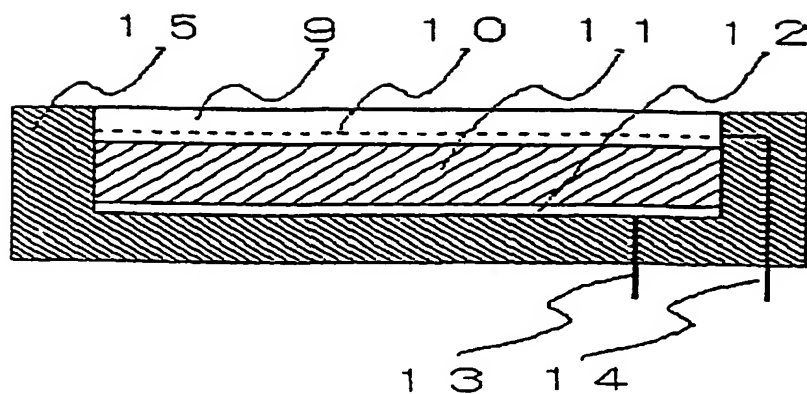


FIG. 3

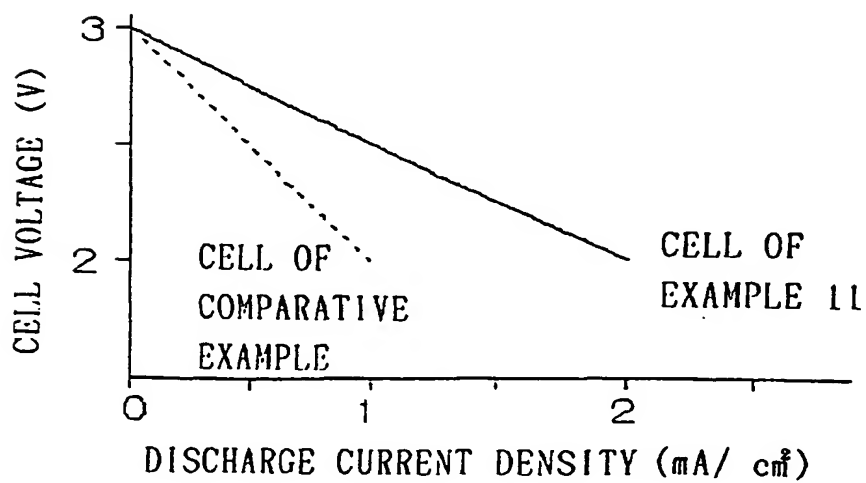


FIG. 4

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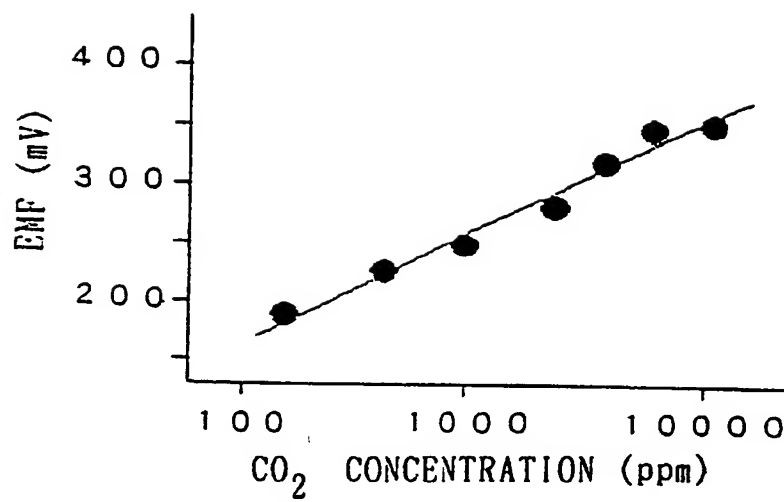


FIG. 5

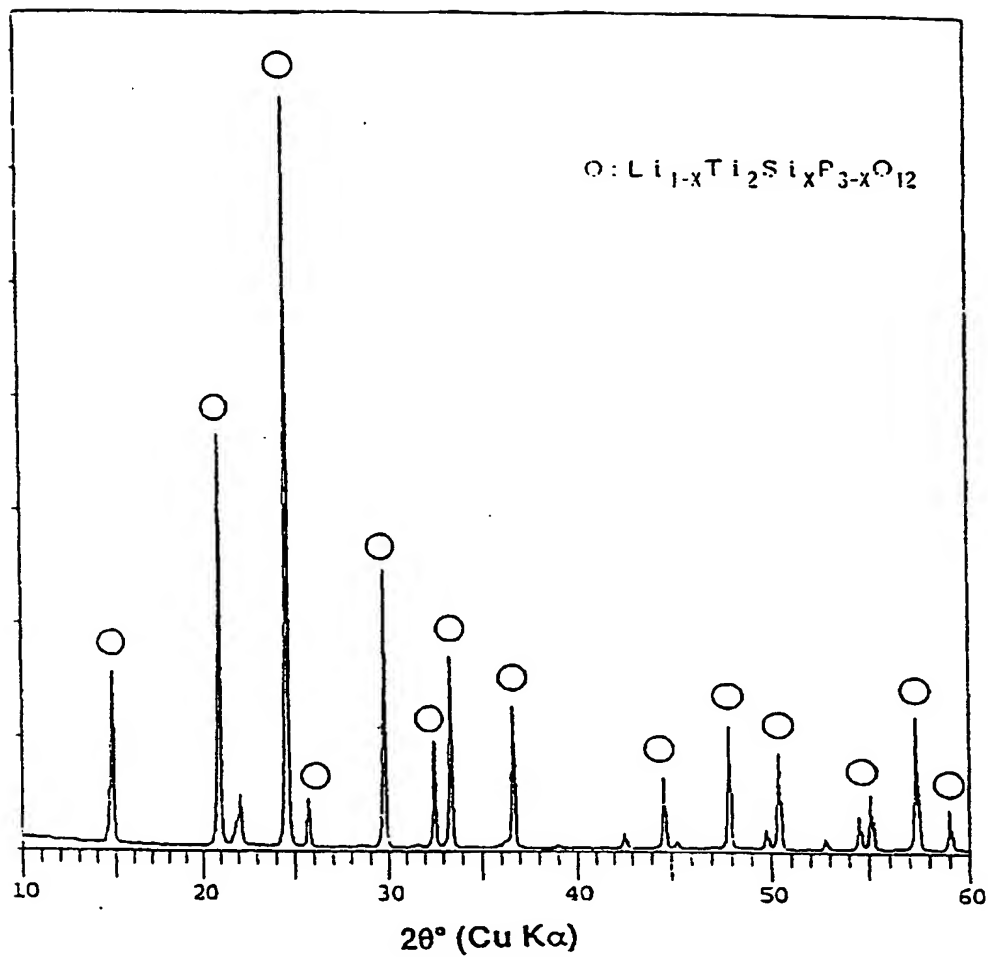


FIG. 6

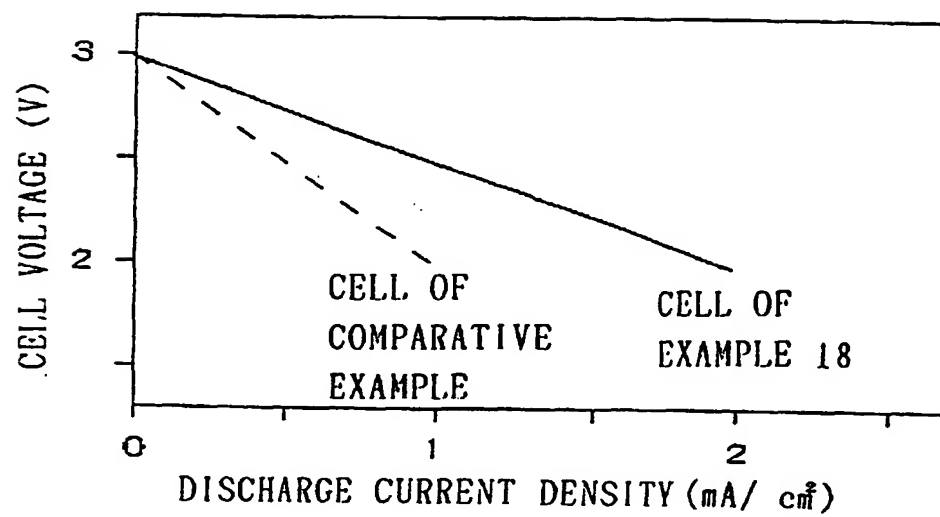


FIG. 7

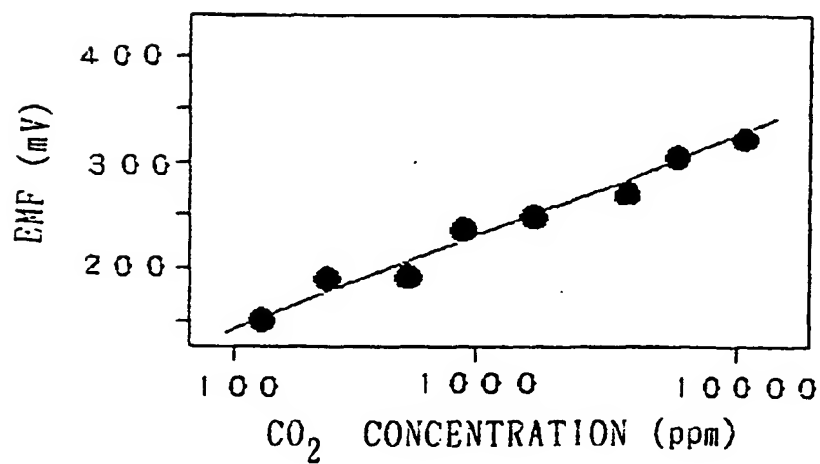


FIG. 8



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(54) **Lithium ion conductive glass-ceramics and electric cells and gas sensors using the same**

(57) There are provided glass-ceramics having a high lithium ion conductivity which include in mol %:

P ₂ O ₅	35 - 40%
SiO ₂	0 - 15%
GeO ₂ + TiO ₂	25 - 50%
in which GeO ₂	0 < - 50%
and TiO ₂	0 - < 50%
ZrO ₂	0 - 10%
M ₂ O ₃ (where M is one or two selected from the group consisting of Al and Ga)	0.5 - 15%
Li ₂ O	10 - 25%

and containing Li_{1+X}M_X(Ge_{1-Y}Ti_Y)_{2-X}(PO₄)₃ (where 0 < X < 0.8 and 0 < Y < 1.0) as a main crystal phase. There are also provided glass-ceramics having a high lithium ion conductivity which include in mol %

P ₂ O ₅	32 - 40%
SiO ₂	7 - 14%
TiO ₂	38 - 45%
Li ₂ O	10 - 18%

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and containing $\text{Li}_{1+X}\text{Ti}_2\text{Si}_X\text{P}_{3-X}\text{O}_{12}$ (where $X > 0$) as a main crystal phase. There are also provided solid electrolyte for an electric cell and a gas sensor using the lithium ion conductive glass-ceramics, and a solid electric cell and a gas sensor using the glass-ceramics.



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 97 11 8218

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	IMANAKA N ET AL: SOLID STATE IONICS, vol. 62, no. 3/4, 1 August 1993, pages 167-171, XP000415545 * the whole document *	1-3,5,6	C03C4/14 C03C10/00
P,A	PATENT ABSTRACTS OF JAPAN vol. 097, no. 010, 31 October 1997 & JP 09 142874 A (OHARA INC), 3 June 1997, * abstract *	1-3,5,6	
A	PATENT ABSTRACTS OF JAPAN vol. 017, no. 513 (C-1111), 16 September 1993 & JP 05 139781 A (RES DEV CORP OF JAPAN), 8 June 1993, * abstract *	1-3,5,6	
A	H. AONO ET AL: BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN., vol. 65, no. 8, 1992, TOKYO JP, pages 2200-2204, XP002057073 * the whole document *	1-3,5,6	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C03C H01M
A	SHI-CHUN LI ET AL: SOLID STATE IONICS, vol. 28 - 30, no. PART 02, 1 September 1988, pages 1265-1270, XP000169535	1-3	
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-/--			
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 26 February 1998	Examiner Kuehne, H-C
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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European Patent
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EUROPEAN SEARCH REPORT

Application Number
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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	ZU-XIANG LIN ET AL: SOLID STATE IONICS, vol. 18/19, 1986, pages 549-552, XP002057074 * the whole document * -----	1-3,5,6	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
The present search report has been drawn up for all claims.			
Place of search BERLIN		Date of completion of the search 26 February 1998	Examiner Kuehne, H-C
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

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EP 97118218

CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing more than ten claims.

- ☐ All claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for all claims.
- ☐ Only part of the claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid, namely claims:
- ☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.



LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirement of unity of invention and relates to several inventions or groups of inventions,

namely:

1. Claims: 1-3,5-8

Lithium ion conductive glass ceramic comprising in mol%:

P2O5 35-40,
SiO2 8-15,
GeO2 + TiO2 25-50 ($0 < \text{GeO}_2 < 50$ and $0 < \text{TiO}_2 < 50$),
ZrO2 8-10,
M2O3 (M is Al or Ga) 0.5-15,
LiO2 10-20

and has

$\text{Li}_{1-x}\text{M}_x(\text{Ge}_{1-y}\text{Ti}_y)_2\text{-x}(\text{PO}_4)_3$ ($0 < x \leq 0.8$ and $0 < y < 1.0$) as a main crystal phase and its use.

2. Claim : 4

Lithium ion conductive glass ceramic comprising in mol%:

P2O5 32-40,
SiO2 7-14,
TiO2 38-45,
LiO2 10-18

and has

$\text{Li}_{1-x}\text{Ti}_2\text{Si}_x\text{P}_3\text{-xO}_{12}$ ($x > 0$) as a main crystal phase.

- ☐ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.
- ☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respects of which search fees have been paid, namely claims:
- ☒ None of the further search fees has been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims.

namely claims 1-3,5-8

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United States Patent [19]

Bates

[11] Patent Number: 5,314,765

[45] Date of Patent: May 24, 1994

[54] PROTECTIVE LITHIUM ION CONDUCTING CERAMIC COATING FOR LITHIUM METAL ANODES AND ASSOCIATE METHOD

[75] Inventor: John B. Bates, Oak Ridge, Tenn.

[73] Assignee: Martin Marietta Energy Systems, Inc., Oak Ridge, Tenn.

[21] Appl. No.: 137,285

[22] Filed: Oct. 14, 1993

[51] Int. Cl.⁵ H01M 10/40

[52] U.S. Cl. 429/194; 429/218; 429/48; 29/623.5

[58] Field of Search 429/218, 194, 48, 197; 29/623.5

[56] References Cited

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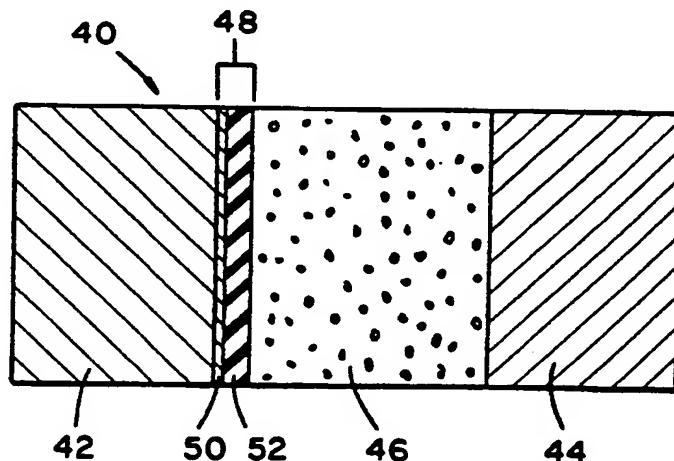
Primary Examiner—Anthony Skapars

Attorney, Agent, or Firm—Michael E. McKee; J. Donald Griffin; Harold W. Adams

[57] ABSTRACT

A battery structure including a cathode, a lithium metal anode and an electrolyte disposed between the lithium anode and the cathode utilizes a thin-film layer of lithium phosphorus oxynitride overlying so as to coat the lithium anode and thereby separate the lithium anode from the electrolyte. If desired, a preliminary layer of lithium nitride may be coated upon the lithium anode before the lithium phosphorous oxynitride is, in turn, coated upon the lithium anode so that the separation of the anode and the electrolyte is further enhanced. By coating the lithium anode with this material lay-up, the life of the battery is lengthened and the performance of the battery is enhanced.

15 Claims, 1 Drawing Sheet



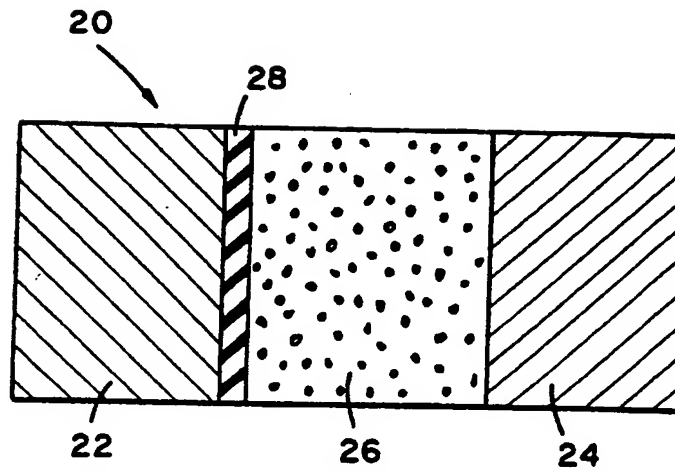


Fig. 1

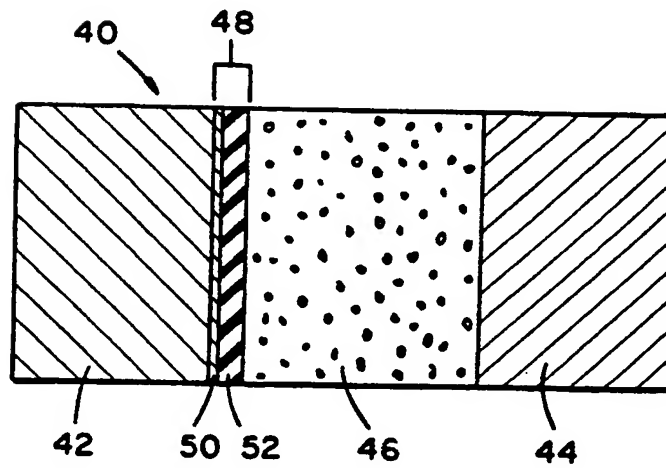


Fig. 2

PROTECTIVE LITHIUM ION CONDUCTING CERAMIC COATING FOR LITHIUM METAL ANODES AND ASSOCIATE METHOD

BACKGROUND OF THE INVENTION

This invention relates generally to batteries, and relates more particularly, to the structure and methods of construction of rechargeable lithium batteries.

Heretofore, the life and performance of lithium batteries have been limited by two major factors. The first of such factors relates to the occurrence of a chemical reaction between the liquid organic or polymer electrolyte and the lithium anode so that a resistive film barrier forms upon the anode. This film barrier increases the internal resistance of the battery and lowers the amount of current capable of being supplied by the battery at the rated voltage.

The second of such factors relates to the undesirable consequences which can result from repeated cycling of the battery. More specifically, battery cycling is at least partly responsible for the dendritic growth of Li on the anode and the formation of a passivating powder-like substance commonly referred to as "dead" lithium at the surface of the lithium anode, either of which can adversely affect the efficiency of the battery. In addition to reducing efficiency, the Li dendrites may grow large enough to touch the cathode through the electrolyte and thereby short the battery.

It is an object of the present invention to provide a new and improved lithium battery structure which circumvents the aforescribed limitations and an associated method of making the battery.

Another object of the present invention is to provide such a battery having a structure which reduces the likelihood of the occurrence of an undesirable chemical reaction between the electrolyte and the lithium anode of the battery.

Still another object of the present invention is to provide such a battery having a structure which prevents the formation of Li dendrites or passivating "dead" lithium at the anode surface.

SUMMARY OF THE INVENTION

This invention resides in a battery having a cathode, a lithium anode, and an electrolyte disposed between the cathode and anode, and a method of making the battery.

The battery of the invention includes a layer of lithium phosphorus oxynitride overlying so as to coat the lithium anode so that the lithium anode is separated from the electrolyte by the lithium phosphorus oxynitride layer. The method of the invention includes, during a battery-making process, a step of depositing a film of lithium phosphorus oxynitride over the lithium anode prior to the positioning of the electrolyte material adjacent the anode so that in the resultant battery, the lithium phosphorous oxynitride is interposed between the lithium anode and the electrolyte.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic cross-sectional view of one embodiment of a battery within which features of the present invention are incorporated.

FIG. 2 is a view similar to that of FIG. 1 of another embodiment of a battery.

DETAILED DESCRIPTION OF AN ILLUSTRATIVE EMBODIMENT

Turning now to the drawings in greater detail, there is shown in FIG. 1 a schematic representation of a rechargeable lithium battery, generally indicated 20, within which features of the present invention are employed. The battery 20 includes a lithium anode 22, a cathode 24 and an electrolyte 26 disposed between the anode 22 and cathode 24. As will be described herein, the anode 22 is prevented from directly contacting the electrolyte 26 by means of a protective film 28 overlying so as to coat the anode 22.

The present invention is envisioned as being well-suited to rechargeable lithium batteries in which dendrite formation and/or reaction of the electrolyte with the lithium anode can degrade the battery performance. However, the principles of the present invention can be variously applied.

The components of the battery 20 may each be fabricated and/or assembled by any of a number of construction techniques. In the interests of the present invention, the lithium anode 22 may take the form of a relatively thick foil or sheet of lithium metal. The cathode 24 can be comprised of V_2O_5 , V_3O_8 , V_6O_{13} , $LiCoO_2$, $LiMn_2O_4$, TiS_2 or any of a number of other lithium intercalation compounds either as a single phase or mixed with a polymer electrolyte and/or graphite or other electronic conductor. The electrolyte layer 26, on the other hand, can be comprised of a solid organic polymer containing an inorganic lithium salt or an organic liquid containing a dissolved lithium salt.

In the depicted FIG. 1 embodiment 20, the protective film 28 is comprised entirely of a layer of lithium phosphorus oxynitride, a material developed by the assignee of the present invention. This material is a solid ceramic material capable of conducting lithium ions there-through. During the formation of the battery 20, the protective thin film 28 can be deposited upon the anode 22 by either rf magnetron sputtering of Li_3PO_4 in the presence of pure nitrogen (N_2) or by rapid electron beam evaporation of Li_3PO_4 in the presence of pure N_2 . Each of these types of deposition processes, i.e. the magnetron sputtering and the electron beam evaporation, are well known so that a more detailed description is not believed to be necessary. A film 28 having a thickness of between 0.1 and 0.5 μm provides satisfactory protection of the lithium anode.

With reference to FIG. 2, there is schematically illustrated another battery embodiment, generally indicated 40, within which features of the present invention are embodied. The battery 40 includes a lithium anode 42, a cathode 44 and an electrolyte 46 disposed between the anode 42 and cathode 44. As is the case with the battery 20 of FIG. 1, the anode 22 is prevented from directly contacting the electrolyte 46 by means of a protective film 48 overlying so as to coat the anode 42.

The protective film 48 of the FIG. 2 battery 40 includes two layers 50, 52 superposed upon the lithium anode 42. The first layer 50 of these layers, i.e. the layer which directly contacts the anode surface, is comprised of a solid film of lithium nitride (Li_3N), while the second layer 52 of these layers is comprised of a solid film of the aforementioned lithium phosphorus oxynitride. During a battery-making operation, the first layer 50 of Li_3N is formed over the lithium metal anode by either controlled exposure of the anode to N_2 at temperatures

from about 30° to 100° C., electron beam evaporation of Li_3N , or by magnetron sputtering of Li_3N in N_2 .

A purpose served by the formation of the Li_3N layer 50 is that the layer 50 coats the surface of the lithium anode 42 in a manner which reduces the likelihood of (undesirable) oxidation of the lithium metal of the anode 42 during fabrication of the battery 40. Thus, it may be desired to include the Li_3N layer 50 as a protective measure during the battery fabrication process, rather than a means to enhance battery performance. A film thickness of the layer 50 of between about 0.05 and 0.1 μm is satisfactory for the purpose served by the layer 50.

During the formation of the battery 20, the second layer 52 of the protective thin film 48 can be deposited upon the first layer 50 by either rf magnetron sputtering of Li_3PO_4 in the presence of pure nitrogen (N_2) or by rapid electron beam evaporation of Li_3PO_4 in the presence of pure N_2 . By way of example, the layer 52 may possess a film thickness of between about 0.1 and 0.5 μm .

The aforescribed protective films 28 (FIG. 1) and 48 (FIG. 2) are advantageous in that each film protects the corresponding anode 22 or 42 from direct contact with the electrolyte 26 or 46. By preventing such direct contact, the likelihood of a film barrier-forming chemical reaction is significantly reduced, and the formation of dendritic growth of Li or the passivating "dead" Li upon the anode due to the cycling of the battery is significantly reduced. Moreover, by reducing the likelihood of the formation of a reaction-spawned film barrier (which is resistive in nature), the longer the battery will be capable of supplying the desired current at the rated voltage. Still further, by preventing the dendritic growth of Li on the anode and preventing the formation of "dead" lithium upon the anode surface, the efficiency of the battery will not be adversely affected by these factors.

Yet still further, the aforescribed films 28 and 48 do not appreciably effect the performance of the batteries in an adverse manner. This fact has been supported by tests involving a 0.25 μm thick coating of lithium phosphorus oxynitride over the lithium anode in a lithium cell of 2.5 V. During such tests, this test battery sustained a current density of 10 mA/cm^2 with only a 5% drop in voltage at a temperature of 25° C. due to the protective coating. These test results were based upon a measured electrolyte resistivity at 25° C. of $5 \times 10^5 \text{ ohm-cm}$.

It will be understood that numerous modifications and substitutions can be had to the aforescribed embodiments without departing from the spirit of the invention. Accordingly, the aforescribed embodiment is intended for the purpose of illustration and not as limitation.

I claim:

1. In a battery including a cathode, a lithium anode, and an electrolyte interposed between the cathode and anode, the improvement comprising:

a protective film including a layer of lithium phosphorus oxynitride overlying and coating the lithium anode so that the lithium anode is separated from the electrolyte by the lithium phosphorus oxynitride layer.

2. The improvement as defined in claim 1 wherein the thickness of the layer of lithium phosphorus oxynitride of the protective film is between about 0.1 and 0.5 μm .

3. The improvement as defined in claim 1 wherein the protective film further includes a layer of lithium nitride (Li_3N) disposed between the surface of the lithium anode and the layer of lithium phosphorus oxynitride.

4. The improvement as defined in claim 3 wherein the thickness of the layer of lithium nitride of the protective film is between about 0.05 and 0.1 μm .

5. The improvement as defined in claim 4 wherein the thickness of the layer of lithium phosphorus oxynitride of the protective film is between about 0.1 and 0.5 μm .

6. A battery structure comprising:

a cathode;

a lithium anode;

an electrolyte disposed between the cathode and the lithium anode; and

a layer of lithium phosphorus oxynitride overlying and coating the lithium anode so that the lithium anode is prevented from contacting the electrolyte by the lithium phosphorus oxynitride layer.

7. The structure as defined in claim 6 wherein the thickness of the layer of lithium phosphorus oxynitride of the protective film is between about 0.1 and 0.5 μm .

8. The improvement as defined in claim 6 wherein the protective film further includes a layer of lithium nitride (Li_3N) disposed between the surface of the lithium anode and the layer of lithium phosphorus oxynitride.

9. The improvement as defined in claim 6 wherein the thickness of the layer of lithium nitride of the protective film is between about 0.05 and 0.1 μm .

10. The structure as defined in claim 9 wherein the thickness of the layer of lithium phosphorus oxynitride of the protective film is between about 0.1 and 0.5 μm .

11. In a battery-forming operation involving the positioning of a lithium anode and an electrolyte material adjacent to one another, the improvement comprising: coating the lithium anode by depositing a film of lithium phosphorus oxynitride over and coating the lithium anode prior to the positioning of the lithium anode and electrolyte material adjacent one another so that when the lithium anode and electrolyte material are positioned adjacent one another in the resultant battery, the lithium phosphorus oxynitride is interposed between the lithium anode and the electrolyte.

12. The improvement as defined in claim 11 wherein the depositing step effects the formation of a lithium phosphorus oxynitride film having a thickness of between about 0.1 and 0.5 μm .

13. The improvement as defined in claim 11 wherein the step of depositing a film of lithium phosphorus oxynitride is preceded by a step of depositing a film of lithium nitride (Li_3N) over so as to coat the lithium anode so that the subsequent step of depositing the film of lithium phosphorus oxynitride coats the Li_3N with the lithium phosphorus oxynitride film.

14. The improvement as defined in claim 13 wherein the step of depositing the film of Li_3N effects the formation of the Li_3N film having a thickness of between about 0.05 and 0.1 μm .

15. The improvement as defined in claim 14 wherein the step of depositing a film of lithium phosphorus oxynitride effects the formation of the lithium phosphorus film of between about 0.1 and 0.5 μm .

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United States Patent [19]

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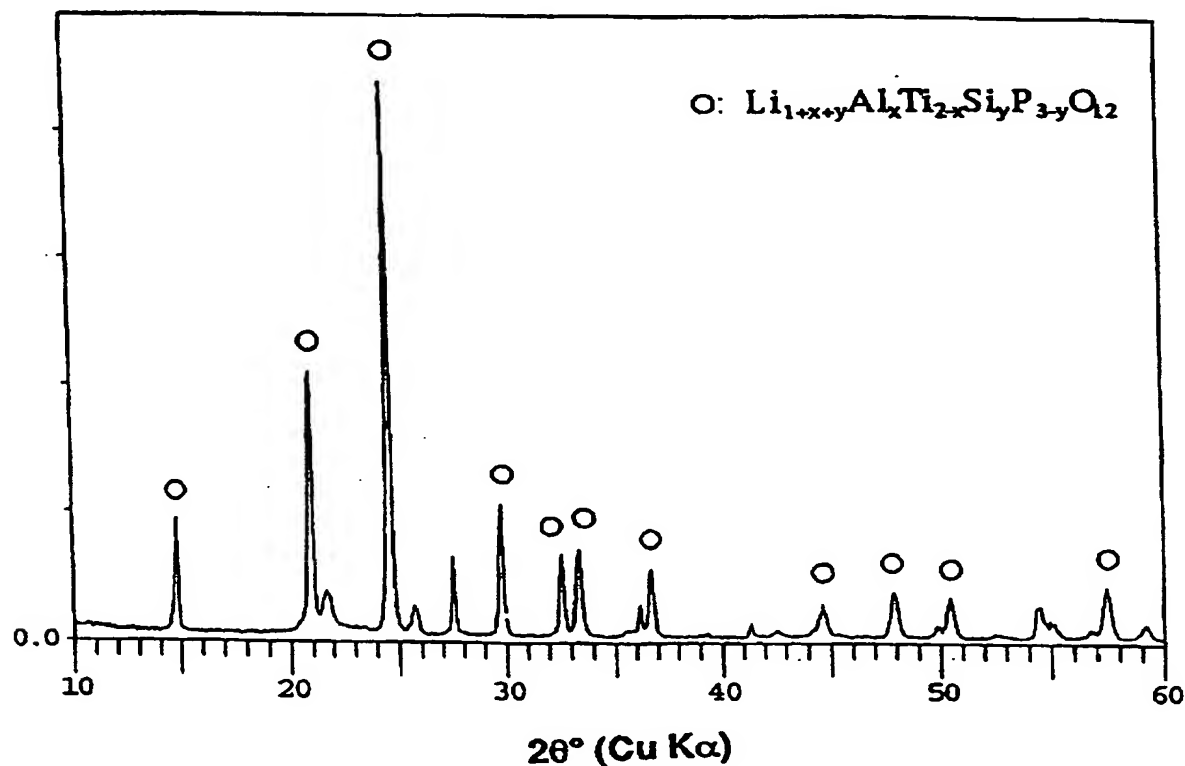
[11] Patent Number: **5,702,995**[45] Date of Patent: **Dec. 30, 1997****[54] LITHIUM ION CONDUCTIVE GLASS-CERAMICS**[75] Inventor: **Jie Fu, Sagamihara, Japan**[73] Assignee: **Kabushiki Kaisha Ohara, Japan**[21] Appl. No.: **741,704**[22] Filed: **Oct. 31, 1996****[30] Foreign Application Priority Data**Nov. 15, 1995 [JP] Japan 7-320971
Apr. 12, 1996 [JP] Japan 8-115694[51] Int. Cl.⁶ **C03C 10/02; C03C 4/14**[52] U.S. Cl. **501/10; 501/4; 501/46; 501/48; 501/73; 252/518**[58] Field of Search **501/3, 4, 10, 46, 501/48, 73; 429/193, 33; 252/518****[56] References Cited****U.S. PATENT DOCUMENTS**4,223,077 9/1980 Taylor 501/4
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Attorney, Agent, or Firm—Hedman, Gibson & Costigan,
P.C.**[57] ABSTRACT**

There are provided glass-ceramics having a high lithium ion conductivity which include in mol %

P ₂ O ₅	38-40%
TiO ₂	25-45%
M ₂ O ₃ (where M is Al or Ga)	5-15%
Li ₂ O	10-20%

and contain $\text{Li}_{1+X}(\text{Al, Ga})_X\text{Ti}_{2-X}(\text{PO}_4)_3$ (where X is 0 to 0.8) as a main crystal phases. There are also provided glass-ceramics having a high lithium ion conductivity which include in mol %

P ₂ O ₅	26-40%
SiO ₂	0.5-12%
TiO ₂	30-45%
M ₂ O ₃ (where M is Al or Ga)	5-10%
Li ₂ O	10-18%

and contain $\text{Li}_{1+X+Y}\text{M}_X\text{Ti}_{2-X}\text{Si}_Y\text{P}_{3-Y}\text{O}_{12}$ (where $0 < X \leq 0.4$ and $0 < Y \leq 0.6$) as a main crystal phase.**8 Claims, 1 Drawing Sheet**



LITHIUM ION CONDUCTIVE GLASS-CERAMICS

BACKGROUND OF THE INVENTION

This invention relates to a lithium ion conductive glass-ceramics suitable for use as all solid electric cell, sensors and electrochemical devices of various types.

Recent development in electronics has brought about high-performance electronic devices of a compact and lightweight design and, as a power source of such electronic devices, development of an electric cell of a high energy density and a long life is strongly desired for.

Lithium has the highest oxidation-reduction potential of Li/Li^+ of all metal elements and has the smallest mass per 1 mol and, therefore, lithium cell can provide a higher energy density than other types of cells. Moreover, if a lithium ion conductive solid electrolyte is used, this electrolyte can be made very thin and, therefore, a cell of a thin film can be formed and increase in energy density per unit volume can thereby be realized.

A lithium ion cell which has been realized to date uses an organic electrolyte solution as its electrolyte and this makes it difficult to achieve a cell of a compact design such as a thin film design. This lithium ion cell has additional disadvantages that it has likelihood of leakage of electrolyte solution and likelihood of spontaneous combustion. If this lithium ion cell is replaced by a cell employing an inorganic solid electrolyte, a wholly solid cell of a high reliability will be realized. For this reason, studies and developments of a solid electrolyte having a high conductivity have been vigorously made for realizing a wholly solid lithium cell. Among known solid electrolytes, Li_2N single crystal (Applied Physics letter, 30(1977) 621-22) and $\text{LiI-Li}_2\text{S-P}_2\text{S}_5$, $\text{LiI-Li}_2\text{S-SiS}_4$ and $\text{LiI-Li}_2\text{S-B}_2\text{S}_3$ glasses (Mat. Res. Bull., 18(1983) 189) have high conductivity of 10^{-3}S/cm or over. These materials, however, have the disadvantages that preparation and handling of these materials are difficult and that decomposition voltage of these materials is so low that, when they are used for a cell, a sufficiently high terminal voltage cannot be obtained.

An oxide lithium solid electrolyte does not have the above described disadvantages and has a decomposition voltage which is higher than 3V and, therefore, it has possibility of usage as a wholly solid lithium cell if it exhibits a high conductivity at room temperature. It is known in the art that conductivity in an oxide glass can be increased by increasing lithium ion concentration. However, there is limitation in increase in the lithium ion concentration even if rapid quenching is employed for glass formation and conductivity of this glass at room temperature is below 10^{-6}S/cm at the highest. An oxide ceramic having the highest conductivity at room temperature is $\text{Li}_{1-x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$. When X is 0.3, the conductivity thereof is $7 \times 10^{-4}\text{S/cm}$ at room temperature (J. Electrochem. Soc., 137 (1990) 1023). Oxide ceramics are superior in conductivity to glasses but have the disadvantages that they require a troublesome process for manufacturing and that they are difficult to form, particularly to a thin film.

In short, the prior art lithium ion solid electrolytes have the problems that they are either low in conductivity, hard to handle, hard to form to a compact design such as a thin film.

It is, therefore, an object of the invention to provide glass-ceramics which have solved these problems and exhibit a very high lithium ion conductivity in the order of 10^{-3}S/cm at room temperature.

SUMMARY OF THE INVENTION

As described above, $\text{Li}_{1-x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ ceramics exhibit conductivity of 10^{-4}S/cm or over at room tempera-

ture. These ceramics, however, have pores and a bad grain boundary which can not be eliminated completely and existence of these pores and grain boundary results in a decrease in conductivity. If, therefore, glass-ceramics including the above crystal are provided, there will be no pores and the grain boundary will be improved and, as a result, a solid electrolyte having a higher conductivity is expected to be provided. Besides, glass-ceramics which share a feature of glass can be easily formed into various shapes including a thin film by utilizing this feature of glass. For these reasons, glass-ceramics are considered to have practical advantages over ceramics made by sintering.

As a result of studies and experiments made by the inventor of the present invention on the basis of the above described basic concept, the inventor has succeeded in obtaining glass-ceramics having a very high lithium ion conductivity in the order of 10^{-3}S/cm at room temperature by producing glasses including the ingredients of the above described crystal and causing the crystal phase to grow from these glasses by heat treating these glasses.

A lithium ion conductive glass-ceramics achieving the above object of the invention comprise in mol %

P_2O_5	38-40%
TiO_2	25-45%
M_2O_3 (where M is Al or Ga)	5-15%
Li_2O	10-20%

and contains $\text{Li}_{1-x}(\text{Al, Ga})_x\text{Ti}_{2-x}(\text{PO}_4)_3$ (where X is 0 to 0.8) as a main crystal phase.

In one aspect of the invention, said glass-ceramics comprise in mol %

P_2O_5	38-40%
TiO_2	30-45%
Al_2O_3	5-15%
Li_2O	10-16%

In another aspect of the invention, said glass-ceramics comprise in mol %

P_2O_5	38-40%
TiO_2	25-45%
Ga_2O_3	5-12%
Li_2O	10-20%
Li_2O	10-20%

The inventor of the present invention has further succeeded in obtaining glass-ceramics having the high lithium ion conductivity in the order of 10^{-3}S/cm at room temperature by producing glasses including ingredients of P_2O_5 , SiO_2 , TiO_2 , M_2O_3 (where M is Al or Ga) and Li_2O and causing a crystal phase of a conductive crystal $\text{Li}_{1-x+y}\text{M}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ to grow from the glasses by heat treating these glasses.

Therefore, in another aspect of the invention, here is provided a lithium ion conductive glass-ceramics comprising in mol %

P_2O_5	26-40%
SiO_2	0.5-12%
TiO_2	30-45%
M_2O_3 (where M is Al or Ga)	5-10%
Li_2O	10-18%

and containing $\text{Li}_{1-x+y}\text{M}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ (where $0 < X \leq 0.4$ and $0 < Y \leq 0.6$) as a main crystal phase.

In this system, SiO_2 is a very important ingredient. By adding SiO_2 , the glass forming range is broadened and, moreover, melting property and thermal stability of the glass are improved and an excellent conductivity in the order of 10^{-3}S/cm can be obtained.

A part of Al or Ga may be replaced by one of such trivalent metal elements such as B, In, Sc, Fe and Cr or one of such divalent metal elements as Mg and Zn. Likewise, a part of Ti may be replaced by Zr and a part of Si may be replaced by Ge. In these cases, however, the amount of Al, Ga, Ti or Si replaced by such metal element should not exceed 5%. If the amount of the replaced metal element exceeds 5%, conductivity will drop significantly.

For improving the melting property of the glass, As_2O_3 , Sb_2O_3 , Ta_2O_5 , CdO or PbO may be added. The amount of such ingredient however should not exceed 3%. If the amount of such ingredient exceeds 3%, conductivity of the glass-ceramic will decrease as the amount of addition of the ingredient increases.

A method for manufacturing the conductive glass-ceramics of the $\text{P}_2\text{O}_5\text{-SiO}_2\text{-TiO}_2\text{-(Al}_2\text{O}_3, \text{Ga}_2\text{O}_3)\text{-Li}_2\text{O}$ system will now be described.

Starting materials are weighed at a predetermined ratio and mixed uniformly and the mixed materials are thereafter put in a platinum crucible and heated and melted in an electric furnace. First, gas components coming from the raw materials are evaporated at 700°C . and then the temperature is raised to 1400°C . to 1500°C . and the materials are melted at this temperature for about one to two hours. Then the melt is cast onto stainless steel plate to form a sheet glass. The glass thus produced is thereafter subjected to heat treatment by heating it under a temperature ranging from 680°C . to 800°C . for about twelve hours and subsequently heating it under a temperature which is higher by 200°C . to 350°C . for about twenty-four hours and glass-ceramics containing $\text{Li}_{1+x}\text{M}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ as a main crystal phase and having a high lithium ion conductivity is produced.

This two-step heat treatment method is applicable also to the production of the glass-ceramics of the $\text{P}_2\text{O}_5\text{-TiO}_2\text{-(Al}_2\text{O}_3, \text{Ga}_2\text{O}_3)\text{-Li}_2\text{O}$ system. Conversely, the glass-ceramics of the $\text{P}_2\text{O}_5\text{-SiO}_2\text{-TiO}_2\text{-(Al}_2\text{O}_3, \text{Ga}_2\text{O}_3)\text{-Li}_2\text{O}$ system can be produced by employing the one step heat treatment method described above with respect to the glass-ceramics of the $\text{P}_2\text{O}_5\text{-TiO}_2\text{-(Al}_2\text{O}_3, \text{Ga}_2\text{O}_3)\text{-Li}_2\text{O}$ system.

Examples

Examples of the glass-ceramics made according to the invention will now be described. It should be noted that these examples are illustrative only and the scope of the invention in no way is restricted by these examples.

Example 1

As starting materials, $\text{NH}_4\text{H}_2\text{PO}_4$, TiO_2 , Al(OH)_3 and Li_2CO_3 were used. These starting materials were weighed to constitute a composition of $39\text{P}_2\text{O}_5\text{-}8.5\text{Al}_2\text{O}_3\text{-}39\text{TiO}_2\text{-}13.5\text{Li}_2\text{O}$ in mol %. The materials were mixed uniformly and then put in a platinum crucible and heated and melted in an electric furnace. First, CO_2 , NH_3 and H_2O coming from the raw materials were evaporated at 700°C . Then the temperature was raised to 1450°C . and the materials were melted by heating them at this temperature for 1.5 hour. Thereafter, the melt was cast onto a stainless steel plate to form a uniform sheet glass. The glass was annealed at 550°C . for two hours for removing thermal stress of the glass.

The glass thus produced was cut into specimens each having the size of $20\times 20\text{ mm}$. The specimens of glass were

polished on both surfaces and subjected to heat treatment under various heat conditions. The crystal phase which precipitated in the specimens was determined by the powder X-ray diffraction method. As a result, it was found that the precipitated crystal phase under all heat conditions was $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$. Electrical conductivity of the glass-ceramic was measured within a range from $10^{-2}\text{-}3\times 10^{-7}\text{ Hz}$ by the complex impedance. Resistance of the specimens (sum of grain resistance and grain boundary resistance) was determined from the Cole-Cole Plot and the conductivity was calculated by the equation $\sigma=(t/AR)(1/R)$ (where σ is conductivity, t is thickness of the specimen, A is electrode area and R is resistance of the specimen). As a result, the specimen which was heat treated at 1000°C . for 12 hours exhibited the highest conductivity of $1.3\times 10^{-3}\text{S/cm}$ at room temperature (Table 1, Example No. 1).

Example 2

As the starting materials, $\text{NH}_4\text{H}_2\text{PO}_4$, TiO_2 , Al(OH)_3 , Ga_2O_3 and Li_2CO_3 were used to produce a glass-ceramic by employing the same manner as in Example 1. The crystal phase which grew in specimens of this glass-ceramic was determined to be $\text{Li}_{1+x}(\text{Al, Ga})_x\text{Ti}_{2-x}(\text{PO}_4)_3$. The specimen which was heat treated at 950°C . for 12 hours exhibited the highest conductivity of $1.0\times 10^{-3}\text{S/cm}$ (Table 1, Example No. 2).

TABLE 1

No.	(composition in mol %)	
	Examples	
	1	2
P_2O_5	39	39
TiO_2	39	38
Al_2O_3	8.5	6.5
Ga_2O_3		2.5
Li_2O	13.5	14
conductivity at room temperature (S/cm)	1.3×10^{-3}	1.0×10^{-3}
temperature of heat treatment ($^\circ\text{C}$.)	1000	950
time of heat treatment (Hr)	12	12

Example 3

As starting materials, $\text{NH}_4\text{H}_2\text{PO}_4$, SiO_2 , TiO_2 , Al(OH)_3 and Li_2CO_3 were used. These starting materials were weighed to constitute a composition of $32\text{P}_2\text{O}_5\text{-}8\text{SiO}_2\text{-}41\text{TiO}_2\text{-}5\text{Al}_2\text{O}_3\text{-}14\text{Li}_2\text{O}$ in mol %. The materials were mixed uniformly and then put in a platinum crucible and heated and melted in an electrical furnace. First, CO_2 , NH_3 and H_2O coming from the raw materials were evaporated at 700°C . Then the temperature was raised to 1450°C . and the materials were melted by heating them at this temperature for 1.5 hour. Thereafter, the melt was cast onto a stainless steel plate to form a uniform sheet glass. The glass was annealed at 550°C . for two hours for removing thermal stress of the glass.

The glass thus produced was cut into specimens each having the size of $20\times 20\text{ mm}$. The specimens of glass were polished on both surfaces and subjected to heat treatment at a temperature of 800°C . for 12 hours and then at 1000°C . for 24 hours to produce a dense glass-ceramic. The crystal phase precipitated in the specimens was determined by the powder X-ray diffraction to be $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$.

The glass-ceramic exhibited a very high conductivity of 1.5×10^{-3} S/cm at room temperature (Table 2, Example No. 3).

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 shows an X-ray diffraction pattern of the glass-ceramic of Example 3.

Examples 4-8

Specimens of glass-ceramics were prepared in a manner similar to Example 3. The compositions and conductivities of these specimens as well as the composition and conductivity of Example 1 are shown in the following Tables 2 and 3.

TABLE 2

(composition in mol %)				
Examples				
No.	3	4	5	
P ₂ O ₅	32	33.5	30	
SiO ₂	8	6	10	
TiO ₂	41	42	40	
Al ₂ O ₃	5	5	5	
Ga ₂ O ₃				
Li ₂ O	14	13.5	15	
conductivity at room temperature (S/cm)	1.5×10^{-3}	1.0×10^{-3}	1.2×10^{-3}	

TABLE 3

(composition in mol %)				
Examples				
No.	6	7	8	
P ₂ O ₅	35	32	35	
SiO ₂	4	8	4	
TiO ₂	38	41	38	
Al ₂ O ₃	8		5	
Ga ₂ O ₃		5	3	
Li ₂ O	15	14	15	
conductivity at room temperature (S/cm)	1.1×10^{-3}	1.2×10^{-3}	1.0×10^{-3}	

What is claimed is:

1. Lithium ion conductive glass-ceramics comprising in mol %:

P ₂ O ₅	38-40%
TiO ₂	25-45%
M ₂ O ₃ (where M is Al or Ga)	5-15%
Li ₂ O	10-20%

and containing $\text{Li}_{1-x}(\text{Al}, \text{Ga})_x\text{Ti}_{2-x}(\text{PO}_4)_3$ where $0 < x < 0.8$ as a main crystal phase.

2. Glass-ceramics as defined in claim 1 wherein said glass-ceramics comprise in mol %:

P ₂ O ₅	38-40%
TiO ₂	35-45%
M ₂ O ₃ (where M is Al or Ga)	5-15%
Li ₂ O	10-16%

3. Glass-ceramics as defined in claim 1 wherein said glass-ceramics comprise in mol %

P ₂ O ₅	38-40%
TiO ₂	25-45%
Ga ₂ O ₃	5-12%
Li ₂ O	10-20%

4. Lithium ion conductive glass-ceramics comprising in mol %

P ₂ O ₅	26-40%
SiO ₂	0.5-12%
TiO ₂	30-45%
M ₂ O ₃ (where M is Al or Ga)	5-10%
Li ₂ O	10-18%

30 and containing $\text{Li}_{1+x+y}\text{M}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ (where $0 < x \leq 0.4$ and $0 < y \leq 0.6$) as a main crystal phase.

5. Glass-ceramics as defined in claim 4 wherein said glass-ceramics comprise in mol %:

P ₂ O ₅	26-40%
SiO ₂	0.5-12%
TiO ₂	32-45%
M ₂ O ₃ (where M is Al or Ga)	5-10%
Li ₂ O	10-18%

6. Glass-ceramics as defined in claim 4 wherein said glass-ceramics comprise in mol %

P ₂ O ₅	26-40%
SiO ₂	0.5-12%
TiO ₂	32-45%
Ga ₂ O ₃	5-10%
Li ₂ O	10-18%

7. Glass-ceramics as defined in claim 1 wherein M is Ga.

8. Glass-ceramics as defined in claim 2 wherein M is Ga.

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